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**CONVERSION COATINGS  
FOR ALUMINUM ALLOYS:  
AN ANNOTATED BIBLIOGRAPHY**

SPECIAL BIBLIOGRAPHY  
SB-63-82

DECEMBER 1963

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Compiled by  
JACK B. GOLDMANN

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Work offered in support of NASA Contract NAS 8-5600

*Lockheed*

**MISSILES & SPACE COMPANY**

A GROUP DIVISION OF LOCKHEED AIRCRAFT CORPORATION

SUNNYVALE, CALIFORNIA

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ABSTRACT

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The chemical conversion coatings with which this annotated bibliography is concerned include chromate, phosphate and oxide processes. The resources of Lockheed Missiles and Space Company Technical Information Center were utilized in the preparation and compilation of this survey.

*Letter*

Search completed December 1963.

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## LITERATURE SEARCH CAPABILITY DEFINED

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1. Ades, L. and H. Aronovitz  
Chromating (of zinc or cadmium electrodeposits,  
and of magnesium, copper and aluminum alloys).  
GALVANO (273):469-472, 1959.

Theoretical and practical aspects are considered.

2. Adrena-Werke G. m. b. H., Germany  
PRINTING PLATES. German Patent 1,037,474.  
28 Aug 1958.

The title materials from aluminum or aluminum alloys are provided with a protective coating by phosphatization.

3. Anderson, R. W.  
Chromating of aluminum and aluminum assembly.  
METAL FINISHING 59(12):63, Dec 1961.

The use of NaOH or acid after assembly should be avoided owing to the danger of entrapment. The use of caustic etch before assembly, followed by degreasing in  $\text{CH}_3\text{OH}$  after assembly, is recommended before applying the conversion coating.

4. Bleiweis, J. L.  
The finishing of light alloys. METAL FINISHING  
49(2):49-55. Feb 1951.

Correlated review, in outline form, of the various processes used for application of inorganic chemical or "conversion" coatings and of plated metallic coatings to aluminum and magnesium and their alloys. Purpose, nature of coating, treatment cycle, and comments on each specific type.

5. Brusentsova, V. N., V. P. Krylov and E. G. Savel'eva  
Chromium plating of aluminum alloys for increased  
wear resistance. TRUDY. GOSUDARST. SOYUZ.  
NAUCH-ISSEDOVATEL. TRAKTOR. INST. (18):  
3-22, 1959. (In Russian).

To establish a chromium plating procedure for Aluminum alloys, various methods of surface preparation were investigated. Anodizing of the aluminum in a solution of



chromic anhydride resulted in good adherence of chromium coatings 0.15-0.17 mm. thick; wear resistance, tested in laboratory conditions, was good. Further investigations will be conducted on chromium-plated aluminum-alloy engine cylinders.

6. Castell, W.  
Iridite No. 14 for protecting aluminum alloys.  
MODERN METALS 10(10):42, 44-44. Nov  
1954; also STEEL 136(26):96-97. 27 Jun 1955.

Iridite process applied by Lockheed Aircraft Corp produces complex chromium-chromate film rather than oxide or phosphate. Excellent corrosion resistance provided by Iridite No. 14. Best results in protecting 7075 alloy achieved with this process. Equipment and processing details. Cost savings.

7. Chromium plating directly on to aluminum and  
its alloys. GALVANO (113):10-11, 1946.

Some operational procedures, including solution compositions, are given.

8. Course for the electroplater. Coloring of  
aluminum and aluminum alloys. GALVANOTECHNIK  
UND OBERFLÄCHENSCHUTZ 3(8):29-30.  
Aug 1962. (In German)

A review of colored conversion coatings (MBV type and chromate).

9. Crandell, M. G.  
Surface protection via phosphate coatings.  
CANADIAN CHEMICAL PROCESSING  
35(12):994-996, 998-999, Dec 1951.

Corrosion prevention, paint adherence and quality and appearance of finished product is improved by phosphate treatment of metal surface. Bonderite, based on the process in which insoluble phosphate coating is deposited on metal surface, has given rewarding results in many plants. Coating for aluminum and its alloys. Bonderite as aid in drawing... aluminum. Parco compound is effective rust preventative.

10. Eder, H. and S. Bloeck  
 ORGANOSILICON CORROSION-RESISTANT  
 COATINGS FOR METALLIC SURFACES.  
 (Assigned to Wacker-Chemie G. m. b. H.,  
 Burghausen, Germany) U. S. Patent 3,101,277  
 (Cl. 117-132). 20 Aug 63. 4 p. (Ger.  
 Appl. Apr 30 1958).

Clear, hard, adherent corrosion-resistant coatings are obtained on aluminum... alloys by heating above 350° a film, applied by spraying, brushing, etc., a solvent such as xylene, benzene, or iso-PrOH, containing about 10% by weight silane having about equal parts organic substituent and Si, and the formula  $R_n H_m Si(OR')_{4-n-m}$ , where R is a univalent hydrocarbon radical which may be halogenated but is free of aliphatic unsaturation, R' is H or alkyl, m is 0-1, and n is 0.9-1.2; or the solvent may contain about 10% siloxane derived from such a silane by hydrolysis and condensation, either or both of which operations may be partial. Many suitable silanes are listed, and methods for their hydrolysis are outlined. Various additives such as  $H_3PO_4$ ,  $FeCl_3$ , and organometallic compounds such as alcoholates or chelates may be used to promote hydrolysis. When aluminum specimens 10 mils thick were dipped in a 10% solution of  $Me(MeO)_3Si$  by weight in benzene and heated 30 minutes at 500° they were not attacked by concentrated HCl in 3 hours; and when aluminum collapsible tubes were coated with an iso-PrOH solution containing  $MeSi(OEt)_3$  6.6,  $Me_2Si(OEt)_2$  2.4, and Bu titanate 1% by weight, annealed at 600°, and fumed with 1:1 HCl in  $H_2O$ , 15-16 minutes were required to evolve 1-3 cc.  $H_2$ /17 cm.<sup>2</sup>; whereas without the coating about 1.5 minutes was required under the same conditions.

11. Eggebraaten, V. L. and L. J. Walker  
 Properties of chromate coatings: investigation by radio chemistry. METAL FINISHING  
 60(9):56-58, 63. Sep 1962.

The radioisotope  $S^{35}$ , which was found to co-deposit with chromium, proved to be a more convenient tracer than  $Cr^{51}$ . Using  $S^{35}$ , relative coating thickness determination could be made on a proprietary chromating bath, which produced colorless, thin coatings on aluminum. It was determined that the pH of the bath was important in controlling coating thickness.

12. Fishlock, D. J.  
Chromate and phosphate treatments for corrosion protection. - I. CORROSION PREVENTION AND CONTROL 6(8):42-46, 51. 1959.

The production of such coatings on... aluminum... is described.

13. Fishlock, D. J.  
Chromate and phosphate treatments for corrosion protection. - II. CORROSION PREVENTION AND CONTROL 6(12):42-47, 58. 1959.

The reaction of the metal with the phosphate bath, after-treatments, and methods of measuring film thickness are discussed. Phosphating of... aluminum is described in more detail.

14. Fishlock, D. J.  
Chromate conversion treatments. - I. PRODUCT FINISHING 11(11):53-62. 1958.

A survey.

15. Fishlock, D. J.  
Chromate conversion treatments. - II. PRODUCT FINISHING 12(2):87-93, 116. 1959.

A review.

16. Fishlock, D. J.  
Chromate conversion treatments. - III. PRODUCT FINISHING 12(10):76-86. 1959.

Special chromating processes applicable to aluminum... are reviewed.

17. Flusin, F.  
Surface treatment of aluminum alloys used in  
architecture. REVUE D'ALUMINUM 39(296):  
363-373. Mar 1962. (In French)

Corrosion pitting led to the development of protective surface treatments such as anodizing, conversion treatments and coatings of paint, lacquer, varnish or plastic film.

18. Fris-Gacosa, T. and O. Korelic  
Control and regeneration of baths for phosphate  
treatment of aluminum and aluminum alloys.  
KEMIJA U INDUSTRIJI (ZAGREB) 10:205-209.  
1961. (In Croatian with German and English  
summary); also in JOURNAL OF APPLIED  
CHEMISTRY 12(5):i-511. May 1962. (English  
summary)

Acid baths containing  $\text{PO}_4^{3-}$ ,  $\text{F}^-$  and  $\text{CrO}_4^{2-}$  ions for Alodine surface treatment were investigated. One type contained  $\text{H}_3\text{PO}_4$  ( $d = 1.7$ ) 37 m;  $\text{CrO}_3$  10 g and  $\text{NH}_4\text{F}$  3.7 g/l of water, the other 55 ml, 22 g and 4.35 g of the above plus  $(\text{NH}_4)_2\text{HPO}_4$  2.2 g/l. Methods for analytical control of  $\text{H}_3\text{PO}_4$ ,  $\text{CrO}_3$  and  $\text{F}$  content of the repeatedly used baths were devised. Surface treatment of Al and Al-Mg and Al-Cu-Mg alloys is briefly outlined. Regeneration was studied. Control of  $\text{F}^-$  content by additions of  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{HF}_2$  or 40% HF were tested. It is sufficient to control  $\text{H}_3\text{PO}_4$  and  $\text{CrO}_3$  content once every 300 sq dm/l. Additions of 2 g of 40% HF per litre fresh (50 sq dm/l) bath were recommended.

19. Heinzelman, E., Jr.  
Surface conversion coatings (for metals).  
PRECISION METAL MOLDING 21(5):  
74-75. May 1963.

The application of conversion coatings, especially phosphate and chromate coatings, and their application to treated metal surfaces are reviewed. Surface-preparation methods and apparatus for application of the finishes are described.

20. Hénuset, G.

Alodine coated 'Bordal' dispatch hall. REVUE  
L'ALUMINUM 40(310):634-635. 1963. (In  
French)

Description of a large dispatch hall of Alodine treated aluminum alloy at Cegedur de Chambéry, France.

21. Here are the advantages of conversion coatings.  
PRECISION METAL MOLDING 15(12):54-55,  
57. 1957.

A general account of the chemistry of chromate and phosphate coatings. Results of salt-spray tests are given.

22. Homer, H. J. and J. R. Whitacre  
NICKEL AND CHROMIUM COATINGS BONDED  
TO ALUMINUM WITH LEAD. (Assigned to  
Commonwealth Engineering Co. of Ohio) U.S.  
Patent 2,913,813. 24 Nov 1959.

Aluminum and aluminum-base alloys are degreased and coated in a nitrogen or argon atmosphere in a closed container first with Pb from  $\text{PbEt}_4$  vapor at 600-800° F, and subsequently with nickel or chromium from carbonyl vapor at 350-800° F. Pb is deposited to about 1 mil thickness pm an oxidized aluminum surface during 10 minutes from nitrogen carrying 120 drops/min.  $\text{PbEt}_4$  and flowing at 0.25 cu. ft./min. An adherent plastic film is formed. The gases are drawn through the apparatus at low pressure with a vacuum pump. Later the carbonyl is drawn through in nitrogen at higher pressure approaching atmosphere, with the Pb-coated surface at a lower temperature. In 2-3 min. a 1-mil nickel coating is deposited on the Pb. The nickel coating is bright, resistant to corrosion, and adherent without fracture or peeling.

23. Hooper, A. F., J. C. George and E. E. Keller  
CORROSION RESISTANCE, ELECTRICAL CONDUCTIVITY AND ADHESION CHARACTERISTICS ON MATERIAL - COATINGS AND ADHESION CHARACTERISTICS. General Dynamics/Convair, San Diego, Calif. Rept. no. 8926-033. 10 Mar 1960. 19 p. (Contract AF 04(645)4) ASTIA AD-287 149. (Available from Office of Technical Services, Washington, D. C. \$2.60)

Twelve commercial chemical conversion coatings for aluminum, which conform with Mil-C-5541 requirements, were evaluated when applied to 2024-T3 clad and bare, and 7075-T6 clad and bare aluminum alloys. Salt spray, 100% relative humidity and atmosphere testing were done with coated, coated and lacquered, and galvanically coupled (Type 301 stainless steel) specimens. The electrical conductivity of the various coating was determined by resistance measurement. Point adhesion was determined by impact shock resistance methods. Wide variations were not found in the corrosion protection afforded by the several materials although Alodine 600 offered a slight advantage. Appreciable reductions in the electrical conductivity of surfaces resulted from chemical conversion film application. These reductions tended to be specific with aluminum alloy surface responding best to a specific proprietary coating. Impact shock tests with a wash prime-ZnCrO<sub>4</sub> laquer primer-lacquer topcoat paint system indicated better adhesion with Alodine 1000 and Bonderite 710 chemical films.

24. Hooper, A. F., J. C. George and E. E. Keller  
LONG TERM EFFECTIVENESS IN MARINE ATMOSPHERES. General Dynamics/Convair, San Diego, Calif. Rept. on Material - Finishes and Coatings - "Touch-Up" Corrosion Preventatives. Rept. no. 8926-131. 29 Apr 1959. 7 p. (Contract AF 33-(657)8926) DDC AD-402 163. (Available from Office of Technical Services, Washington 25, D. C. \$1.10).

The effectiveness of 10% chromic acid solution, Alodine 1200, Iridite 14, and Bonderite 710 when applied to clad 7075-T6 aluminum alloy sheet provided with stainless steel metal screws and Huck lockbolts, in retarding industrial-marine atmosphere corrosion was checked. Ten months outdoor exposure of representative test panels revealed that none of the 'touch-up' finishes were effective in retarding corrosive attack for this length of time.

25. Jeremias, B. R.  
CHROMATE-PHOSPHATE COATING. (Assigned  
to Poor & Co., Chicago, Ill) Canadian Patent  
660,443. 2 Apr 1963.

Aluminum or its alloy is contacted with a solution of  $\text{CrO}_3$ ,  $\text{H}_3\text{PO}_4$  and complex acetic acid salt containing combined but undissociated acetic acid derived by replacing water in an acetate salt with acetic acid, and fluoboric acid at  $> 120^\circ\text{F}$ ;  $\text{F}:\text{CrO}_3$  being 0.44-2.2:1 at pH 1-2.

26. Kape, J. M.  
Thicker MBV (modified Bauer-Vogel) coatings.  
INSTITUTE OF METAL FINISHING. TRANS-  
ACTIONS 39(pt.2):75-84. 1962.

Baths based on mixtures of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CrO}_4$  produced chemical conversion coatings on aluminum. Two alkaline solutions were developed in which the pH was controlled closely during processing by additions of lower temperatures. Coatings were produced on various aluminum alloys with these new baths and were compared with other chemical conversion systems in regard to operation, coating thickness, corrosion resistance, color, and voltage breakdown.

27. Keller, H.  
Phosphating and chromating (of aluminum and  
its alloys). ALUMINUM 31(1):4-7. 1955.

The author deals with the various chemical and electrolytic processes for improving the corrosion-resistance of aluminum and/or to act as a key for the application of paint, pointing out the advantages and limitations of each. A description is given in greater detail and the more recently developed and cheaper processes of phosphating and chromating, which are in the nature of pickling processes, leaving only a thin oxide film of maximum thickness  $5\mu$ , and used mainly as a wash primer under paint rather than as a protective coating per se. Methods of application with details of solution used, of each of the better-known processes are given, including Protal, Bonder, Alodine, and Iridite, with some notes on their fields of application and test results.

28. Ketcham, S. J.  
Properties of chemical films on aluminum alloys. In FINISHING OF ALUMINUM; SYM-POSIUM SPONSORED BY AMERICAN ELECTRO-PLATERS SOCIETY, 1961. G. H. Kissin, ed. N. Y., Reinhold, 1963. p. 91-103.

Chemical conversion coatings are discussed with reference to MIL-C-5541. Corrosion resistance paint adhesion and electrical resistance of phosphate; phosphate-chromate and chromate-coatings on various alloys are discussed.

29. Lainer, V. I.  
Chromium plating of aluminum and magnesium alloys. VOPROSY TEORII KHROMIROVAN. AKAD. NAUK LITOVSK. S. S. R. INST. KHIM. I KHIM. TEKHNOL, 1959. p. 151-163. (In Russian).

Successful plating of aluminum, magnesium and their alloys with chromium requires a preliminary plate of a dense, thin Zn layer. The recommended sequence of operations for aluminum involves polishing, degreasing in an organic solvent, cathodic treatment of a weakly alkaline solution (3%  $\text{Na}_2\text{CO}_3$  + 3%  $\text{Na}_3\text{PO}_4$ ), pickling for 5 minutes at 80° in 25%  $\text{H}_2\text{SO}_4$ , purification in 1:1  $\text{HNO}_3$  solution, and, finally, dipping in a solution containing (per litre)  $\text{AnO}$  100,  $\text{NaOH}$  525,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  2,  $\text{NaNO}_3$  1, and  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  10 g. Before chromium plating, the Zn-covered aluminum is plated with copper in a cyanide solution, or with nickel. Thermal treatment of the plated metal is recommended.

30. Lipinski, R. J.  
Organic conversion coatings for improved paint and adhesive bonding to aluminum surfaces. METAL FINISHING 59(9):44-51. Sep 1961.

Advantages of organic conversion films. Mechanism of formation. Theory of environmental bond protection. Lap shear tensile test results on coatings applied to 2024 -T3 Alclad aluminum and paint adhesion peel tests on coatings on 3003-H14 aluminum. Results of metal-to-metal adhesive bonding studies and metal-to-metal climbing drum peel test on 2024-T3 Alclad aluminum.



31. Mansell, R.  
Finishing aluminum. ORGANIC FINISHING  
7(11):31-36, 41; (12):23-29. 1946; 8(1):22-28.  
1947.

The three most common processes used on aluminum surfaces to prevent corrosion and to provide a good base for organic coatings are anodizing, chromatizing, and phosphatizing. Applications for these processes are recommended for the different alloys of aluminum. In addition a review is given also of organic coatings available, miscellaneous chemical finishes and mechanical finishing methods.

32. Marchand, W.  
Chromate conversion coatings on aluminum.  
ELECTROPLATING & METAL FINISHING  
14(12):439-447. Dec 1961.

Author's investigations showed that chromate-fluoride coatings on aluminum radio parts are best produced from solution containing chromic acid, sodium dichromate and sodium fluoride or sodium hydrogen fluoride, but they are still unsatisfactory in appearance. Addition of phosphoric and boric acids followed by dilution enables producing of thin coatings. Attractive in appearance and with excellent resistance to finger printing. Effect of variations in composition of solutions.

33. Murphy, J. F.  
Chemical conversion coatings for aluminum  
alloys. AMERICAN ELECTROPLATERS'  
SOCIETY. TECHNICAL PROCEEDINGS.  
48:60-68. 1961.

Published and proprietary oxide, phosphate, and chromate conversion coatings are reviewed.

34. Murphy, J. F.  
Chemical conversion coatings for aluminum alloys. In FINISHING OF ALUMINUM; SYM-  
POSIUM SPONSORED BY AMERICAN ELECTRO-  
PLATERS SOCIETY, 1961. G. H. Kissin, ed.  
N.Y., Reinhold, 1963. p. 68-90.

Properties and applications of conversion coatings are reviewed. Chemical oxidation-, chromate-, and phosphate processes are reviewed. Effect on adhesion of organic coatings is discussed.

35. Murphy, J. F.  
Chemical conversion coatings for aluminum alloys.  
AMERICAN ELECTROPLATERS' SOCIETY. PRO-  
CEEDINGS. 48:60-68. 1961.

A number of chemical coating solutions, both published and proprietary are discussed. Non-proprietary oxide coatings are less expensive than proprietary phosphate and chromate coatings and are more versatile in producing special color effects. However, control requires more care. Crystalline phosphate coatings are especially useful in applications involving composites of aluminum and other metals. Amorphous phosphate coatings has been used extensively as a pre-paint treatment. For some applications the green color of the coating protected by clear lacquer is used. Chromate coatings appear to be replacing phosphate and oxide coatings and are preferred for both bare and painted applications where wear resistance and appearance are not important, chromate coatings may replace anodizing.

36. Newhard, N. H., Jr., and D. Y. Dollman  
COATING BATHS FOR ALUMINUM AND ITS  
ALLOYS. (Assigned to Amchem Products, Inc.,  
Ambler, Pa.) U.S. Patent 2,936,254. 10 May  
1960.

Baths containing  $F^-$ ,  $Cr^{6+}$ , and  $PO_4^{---}$  are made capable of producing uniformly colored, powder-free coatings on aluminum by making up and replenishing in a definite manner with respect to the concentration of fluoride and alkali metal. The amount of alkali metal must be 0.0026-0.0526 mole per g. of fluoride. From 10 to 90 mole % of the alkali metal should be K. In replenishing the bath, the alkali metal content should be restored in the approx. K; NA mole ratio of 2:1. For each g. of fluoride added, the total amount of alkali metal should be 0.0065-0.455 mole. A glassy, lacquerlike coating is produced when the bath contains 1-5 g. cryolite. A

A typical bath contains  $\text{CrO}$  14.4,  $\text{NaHF}_2$  9.26,  $\text{KHF}_2$  6.02,  $\text{Na}_3\text{AlF}_6$  3.17 g., 50%  $\text{Al}(\text{H}_2\text{PO}_4)_3$  332.0, 75%  $\text{H}_3\text{PO}_4$  36.3 ml., and water to make 1 litre. Under these conditions, any precipitate which forms is  $\text{K}_2\text{NaAlF}_6$ . A green lacquerlike coating is formed from this bath by dipping at  $100^\circ\text{F}$ ., the treating time being approximately 5 minutes.

37. Noonan, J. D. and J. E. Loughlin  
 COLORING ALUMINUM. (Assigned to  
 Allied Chemical Corp., New York, N. Y.)  
 U.S. Patent 2,989, 427. 29 Apr 1961.

A colored layer on aluminum or its alloys is formed by treating in a chromate solution containing a lake forming substrate and dyeing with a cationic dye to form a water-insoluble lake.

38. Oppen, D.  
 Modern processes for the chemical surface treatment of aluminum and aluminum alloys. ALUMINIUM 38(7):450-455. Jul 1962. (In German)

A discussion of chromating processes for aluminum. Brass-yellow, gold-yellow or bright green coatings are dealt with. Process conditions and applications are given. The chemistry of the process is discussed.

39. Ostrander, C. W.  
 Chromate conversion coatings. MATERIALS IN DESIGN ENGINEERING 52(2):116-120. Aug 1960.

High corrosion resistance of chromate conversion coatings is noted. Their appearance, paint bonding characteristics, abrasion resistance, electrical properties and weldability are discussed. Advantages of applying coatings to... aluminum are described. How to evaluate coatings.

40. Ostrander, C. W.  
Chromate conversion coatings for hot-galvanized surfaces. In 6TH INTERNATIONAL GALVANIZING CONFERENCE, INTERLAKEN, JUNE 1961. PROCEEDINGS. p. 179-186.

The problem of wet-storage stain is reviewed with reference to the current use of chromate-type inhibitors. Chromate coatings offer acceptable results not only with hot-galvanized surfaces but also with electrodeposited Zn and Cd, Zn die-castings Al, Mg, and Ag.

41. Ostrander, C. W.  
Chromate protective coatings. PRODUCT ENGINEERING 23(9):127-129. 1952.

Chromate coatings are applicable to...aluminum...and its alloys, provide protection and a suitable base for paint...Particular properties of the coatings are: (1) a thin, pore-free, gel-like structure with a high corrosion resistance; (2) good sealing power to prevent the lateral spread of corrosion; (3) a high electrical conductivity and weldability (it can be used on assembly parts without affecting electrical characteristics, and its use can obviate cleaning before welding); (4) color ranging from colorless to yellow, bronze, or olive drab, according to thickness and metal base; and (5) it can be used over zinc plating to provide a finish similar to chromium plate, or it can be dyed.

42. Pimbley, G. H.  
CONVERSION COATING FOR ALUMINUM.  
(Assigned to Purex Corp., Ltd., Lakewood, Calif) U.S. Patent 3,066,055. 27 Nov 1962.

Aluminum or aluminum alloy is treated in an acid bath containing Va, Cr, Co, Ni or Cu, a halogen containing anion forming free halogen ion and Cr (VI) or ferricyanide at pH 1.6-3.5.

43. Pimbley, G. H.  
CONVERSION COATINGS FOR ALUMINUM AND ITS ALLOYS. (Assigned to Turco Products, Inc., Wilmington, Calif.) U.S. Patent 2,868,679. 13 Jan 1959.

A process is described for applying chemical conversion coatings to aluminum in which the cation of the treating compound is important to the protective function. The aluminum

dissolving anion is likewise important. The cation group consists of Be, Mg, Ca, Sr, and Ba. The anion groups must contain a halogen and the pH of the bath is 1.3-2.2. A typical formulation consisted of Be(OH<sub>2</sub>) 3.27, CrO<sub>3</sub> 7.60, 40° Be. HNO<sub>3</sub> 0.84, NaBF<sub>4</sub> 3.78, Na<sub>2</sub>MoO<sub>4</sub> 1.12 g., and water to make 1 litre. This solution imparted excellent corrosion resistance to aluminum and aluminum alloys as shown by salt-spray tests. A more economical formulation contained CaCrO<sub>4</sub> 11.90, NaBF<sub>4</sub> 3.78, NaMoO<sub>4</sub> 1.12, and 40° Be. HNO<sub>3</sub> 11.00g., plus water to make 1 litre. Other formulations which provide variations in color and appearance are given.

44. Pimbley, G. H.  
CORROSION-RESISTANT COATINGS FOR ALUM-  
INUM. (Assigned to Turco Products, Inc.,  
Wilmington, Calif.) U.S. Patent 2,948,643.  
9 Aug 1960.

Chemical conversion coatings superior to those obtained by use of the solutions disclosed in the previous patents in uniformity and resistance to corrosion and smearing are formed on aluminum and aluminum alloys by treatment at room temperature with aqueous solutions containing Zn, Cd, or Hg ions, sexivalent Cr, H<sup>+</sup>, and anions containing a halogen, preferably F. The color of the coating is controlled by the pH of the solution. About 0.5-8 g. Zn or Cd, or somewhat less Hg, should be present in the solution per litre, with 0.5-9 g. sexivalent chromium, which should be 0.7-2.5 times the weight of F or Cl present. If the halogen is Br or I, the Cr:halogen ratio may be less. For yellow coatings, the solution pH may be 1.3-2.2, and for colorless coatings 2.3-2.7, the acidity being derived from HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or acid salts, but not H<sub>3</sub>PO<sub>4</sub> or phosphates. Suitable solutions are prepared by dissolving 1-4 oz. gal. of water of a dry mixture containing Zn, Cd, or Hg 5-30, sexivalent Cr 5-35, F 5-25, and a solid acid or acid salt 3-10% by weight. The aluminum surface should first be cleaned, and preferably deoxidized by acid. The treatment is effected by 3-5 min. immersion at 75-95° F., or by 1-2 min. spraying or brushing at 90-100° F. Used solutions are regenerated by adding the same dry mixture used for making the solution in an amount sufficient to restore the original chromium content. Such a mixture may contain any halide, nitrate, or other soluble salt of Zn, Cd, or Hg, CrO<sub>3</sub> or a chromate, and any soluble halide, fluoborate, or fluosilicate, such as Hf, NaF, NH<sub>4</sub>BF<sub>4</sub>, or Na<sub>2</sub>-SiF. A suitable mixture is AnSiF<sub>6</sub>.6H<sub>2</sub>O 48.2, CrO<sub>3</sub> 40, and B<sub>2</sub>O<sub>3</sub> 11.8% by weight. For example, when 1.5 oz. was dissolved in 1 gal water, the pH was 1.3, and aluminum alloys immersed for 3-5 minutes in this solution at room temperature acquired a bright yellow film which resisted salt-spray corrosion for 600 hours. Aluminum alloys similarly immersed in the same solution, after the pH was raised to 2.5 by NH<sub>4</sub>OH, acquired a colorless film, which resisted salt-spray corrosion for 240 hrs.

45. Pimbley, G. H.  
 REMOVING THE COLOR FROM CHEMICAL CON-  
 VERSION COATINGS ON ALUMINUM. (Assigned  
 to Turco Products Inc., Wilmington, Calif.) U.S.  
 Patent 2,927,874. 8 Mar 1960.

Yellow corrosion-resistant coatings formed on aluminum or an aluminum alloy by immersion in a solution containing Chromium are rendered substantially colorless, without appreciable impairment of the corrosion resistance, by immersion for 2-30 minutes in a 0.1-10% aqueous solution of K ferrocyanide, hydroquinone,  $H_3PO_3$ , chromic nitrate, Na hypophosphite or thiosulfate, or hydrazine sulfate or hydrate at 70-120° F. The most effective solution for 15-min treatments at 120° F. is one containing 2% hydrazine sulfate. Wetting agents, such as an alkyl aryl sulfonate may be used in these solutions for increased effectiveness. The chemical conversion coatings to be decolorized may be formed by immersion for 2-5 min. in aqueous solutions containing cations of Be, Mg, Ca, Sr, or Ba at 80-90° F. If the aluminum article has an obstructive oxide coating, it first should be immersed for 5-8 min. in 1 litre of aqueous solution containing  $CaCrO_4$  7.94,  $NaBF_4$  2.52,  $NaMoO_4$  40.74, and 40° Be.  $HN_3$  7.34g. to give a deep golden-colored film on the aluminum. The film was rinsed with water and dipped for 4 min. in 0.5% by wt. aqueous hydrazine sulfate solution at 120° F. The conversion coating was rendered substantially colorless and resisted exposure to salt spray for 500 hrs. without corrosion.

46. Pocock, W. E.  
 Chromate coatings for protecting nonferrous  
 metal surfaces. METAL PROGRESS 84(1):  
 100-104. Jul 1963.

Description is given for protection of... aluminum surfaces.

47. Pocock, W. E.  
 Surface protection with chromate coatings.  
 METAL PROGRESS 83(6): 83-87. Jun 1963

Chromate coatings on... aluminum... give protection against corrosion, decorative appeal, and make excellent bases for paint and organic coatings. Production procedures are outlined.

48. Pocock, W. E.  
A survey of chromate treatments. - I. - II.  
METAL FINISHING 52(12):48-51, 1954;  
53(1):80-83, 1955.

(I) The historical development of chromate processes for the treatment of metal surfaces and the nature, methods of application, and general properties of the chromate films are discussed. (II) Chromate treatments for... aluminum... alloys are considered.

49. Porter, F. C.  
Aluminum and corrosion. A review of progress  
in 1960. CORROSION PREVENTION & CONTROL  
8(1):37-43. Jan 1961.

Review of 1960 publications on research and technology covering corrosion mechanisms... Survey of protection and control including... chemical conversion coatings...

50. Pryor, M. J.  
CONVERSION COATING FOR ALUMINUM.  
(Assigned to Kaiser Aluminum & Chemical  
Corp., Oakland, Calif.) U. S. Patent 2,894,865.  
14 Jul 1959.

Aluminum and its alloys are treated in acid solution containing chromate, phosphate and fluorine ions and rinsed in a solution containing a reducing agent that does not give insoluble oxidation products, at pH 3.0-7.0.

51. Pryor, M. J.  
IMPROVEMENT OF CHEMICAL COATINGS ON  
ALUMINUM. (Kaiser Aluminum & Chemical Corp.,  
Oakland, Calif.) U. S. Patent 2,894,865. 14 Jul  
1959.

The treatment of chromate-phosphate-fluoride coatings on aluminum and aluminum alloy products where soluble seivalent chromium ions can be present within the coating, with a solution containing reducing ions as a final reducing rinse, will reduce or eliminate the soluble sexivalent chromium ions. Samples of a louvered screen 12 in. sq. fabricated from 0.008 in. -thick 5052 aluminum alloy (containing 2.5% magnesium) were coated with the above coating in the conventional way. Half of the samples were

rinsed in dilute chromic acid before drying. The other samples were rinsed in a room-temperature solution containing 133 oz  $\text{NaHSO}_3$  in 100 gallon water. The samples were tested by exposure to a marine atmosphere, being partly sheltered to accentuate pick-up of wind-blown deposits. After three months, the samples rinsed with chromic acid showed perforations of the ribs and louvers, while those rinsed in  $\text{NaHSO}_3$  showed no perforations. After 9 months' exposure, the samples rinsed in chromic acid showed an average of 25 broken ribs and louvers per sample. Those rinsed with  $\text{NaHSO}_3$  showed no broken ribs or louvers.

52.

Pyrene Co. Ltd., London, England

## CHROMATE COATING OF ALUMINUM ALLOYS.

British Patent 846,363. 31 Aug 1960.

In the chromate coating of aluminum alloys by treatment with acid aqueous solutions containing fluoride and other ions as well as sexivalent chromium, the accumulation of aluminum or complex aluminum fluoride ions or sludge in the solution, and variations in quality and color of the coatings are prevented by treatment of the solution with a strongly acidic cation-exchange resin which absorbs aluminum and gives up hydrogen ions to the solution in exchange. By continuous circulation of part of the solution through a bed of such resin, the aluminum concentration in the solution may be held at 0.005–0.1%. The acidity of the solution should be sufficient to require 8–100 ml. of 0.1N NaOH solution to neutralize a 10-ml. sample. Styrenedivinylbenzene resins sulfonated with  $\text{H}_2\text{SO}_4$ , and in which 4–8% divinylbenzene is the cross-linking agent, are preferred. They should be in a form containing both hydrogen and other cations, such as Na, K, and  $\text{NH}_4$ , in proportions which do not cause the pH of the treated solution to be changed by contact with the resin. The grain size is preferably 20–50 mesh. When the solution contains phosphate with or without arsenate, to increase the coating rate, the ion concentration should be 3–8%, and the preferred chromate ion concentration is then 1.2–2.6%. Without  $\text{H}_3\text{PO}_4$  or  $\text{As}_2\text{O}_5$ ,  $\text{CrO}_3$  is preferred at 0.07–0.3%. The fluoride concentration should be 0.1–3% and fluoboric acid is the preferred source, the  $\text{H}_3\text{BO}_3$  acting as a buffer. The solutions may also contain 0.02–0.2% ferricyanide ion. The coatings from solutions containing  $\text{PO}_4$  or  $\text{As}_2\text{O}_5$  are green; otherwise they are yellow or brown. When sexivalent chromium in the solution is depleted, the fluoride may not be depleted so much. Satisfactory replenishing solutions contain  $\text{CrO}_3$  5–6 and HF 4–8, or  $\text{CrO}_3$  15–25, Hf 5–8, and  $\text{H}_3\text{PO}_4$  38–48%. The coatings are especially useful as a base for vitreous enamels, since the enamel adheres well to them and resists flaking and cracking, even when enameled samples are cut and bent. Thus, adherent coating suitable for painting were applied on clean strips of aluminum containing 1.2% Mn by spraying at 95° F for 12–23 sec with a solution made from 160 lb of an aqueous concentrate containing  $\text{CrO}_3$  5.4, HF 6.6, and  $\text{H}_3\text{BO}_3$  4.5%, plus 3.5 lb  $\text{K}_3\text{Fe}(\text{CN})_6$ , diluted to 400 gal. with water. During the spraying, 2.3 gal./min. was pumped in through a 4 cu. ft. column of Dowex-50 resin of 20–100-mesh size, which kept the aluminum concentration in the solution from exceeding 0.08%, while 370,000 sq. ft. aluminum surface was sprayed during 56 hours. During this period, the coating color did not change. The solution was replenished with 492 lb. of concentrate and 7 lb.  $\text{K}_3\text{Fe}(\text{CN})_6$ . When the resin bed was saturated, a new one was used, and the saturated bed was regenerated by  $\text{H}_2\text{SO}_4$ .



53. Pyrene Co., Ltd., London, England  
COATINGS ON METALLIC SURFACES. British  
Patent 830,632. 16 Mar 1960.

The addition of a condensed phosphate compound to the standard chromiumfluoride bath for aluminum results in a coating bath useful for both aluminum and iron materials. From 0.01 to 0.5% wt./vol. of the phosphate compound (di-Na pyrophosphate, Tetra-Na pyrophosphate, Na tri-acidic coating both containing  $\text{Cr}^{6+}$  and the F radical produced corrosion resistance and a good base for adhesives and coating on both aluminum and iron and their alloys.

54. Rajagopalan, K. S.  
Chromate treatment of metals. In SYMPOSIUM  
ON ELECTRODEPOSITION AND METAL FIN-  
ISHING, KARAIKUDI, 1957. 1962. p. 182-187.

The author describes the preparation and properties of chromate coatings on Zn, Cd, Cu and its alloys, and on light-metal alloys. Such coatings provide a self-healing base for protective organic substances where it prevents the lifting of the paint film by formation of alkali when paint is applied to untreated metal. Scope and application are described.

55. Renner, K.  
New experiences with aluminum alloys for  
chemical process apparatus. CHEMISCHES  
TECHNIK 3:130-133. 1960. (In German).

Methods for the surface protection of aluminum alloys and the welding and cutting of aluminum alloys under argon are discussed.

56. Rudin, A.  
COATING ALUMINUM OR ALUMINUM-  
ALLOY ARTICLES. (Assigned to Canadian  
Industries Ltd., Canadian Patent 583,410/  
15 Sep 1959.

Protective coatings having good paint-base characteristics are produced on aluminum or aluminum alloys on immersing previously cleaned metal in an aqueous solution containing as essential ingredients,  $\text{F}^-$  0.4,  $\text{PO}_4^{4-}$  7.5, and  $\text{MnO}_4^-$  1.0% by weight,

for 10 minutes at 95°, followed by rinsing in hot water and then in cold distilled water. A typical solution contains distilled water 1900,  $H_3PO_4$  170, M NaF 20, and  $KMn_4$  30 g.

57. Russell, W. S. and J. L. Van Vliet  
CHROMATING OF ALUMINUM AND ITS ALLOYS.  
U. S. Patent 2,928,763. 15 Mar 1960.

A process is described for continuously coating aluminum or aluminum alloys with an adherent coating having good corrosion resistance and utility as an aid in cold-forming operations, and as a base for paint and vitreous enamels. The rate of coating formation increases as the temperature increases; the best temperature is 120–140°. The solutions can be applied by spraying, dipping, or brushing. Aqueous sexivalent chromium solutions operate more efficiently and are substantially nonsludge-forming at pH 0.8–1.5. As aluminum is coated in an aqueous solution of pH 0.3–1.5, containing phosphate, fluoride, and dichromate ions, continued use causes buildup of  $Al^{+++}$  and  $Cr^{+++}$  in the solution. Also, the coating weight gradually decreases. In order to maintain the desired coating weight and appearance the F:– $CrO_3$  ratio is adjusted to well above 0.405:1. For example, an aqueous acidic solution was prepared containing  $PO_4$  5,  $CrO_3$  1.4, and F 0.38%, having a pH of 1.1. The solution was heated to 135° and aluminum panels were immersed in it for 1 min., rinsed and dried. The coating weight was 417 mg./sq. ft. NaOH was added to bring the pH up to 1.9. After coating many panels, the coating weight was found to be only 250 mg./sq. ft. and the solution contained 0.024% Al and 0.008%  $Cr^{+++}$ . A second solution contained  $PO_4$  4,  $CrO_3$  1.5, and F 0.24%, and had a pH of 1.08. Aluminum panels were similarly treated, the fluoride concentration being gradually increased to maintain a coating weight of 250 mg./sq. ft. until 124 sq. ft. of surface and 26.0 g. of 60% HF had been added. Comparable amounts of coating were formed with consumption of approximately 1/3 the amount of fluoride ion required with the solution of pH 1.9.

58. Sal'ko, Kh. A.  
PREVENTING THE CORROSION OF MAGNESIUM,  
ALUMINUM, AND THEIR METAL ALLOYS.  
U. S. S. R. Patent 123,006. 10 Oct 1959.

The metals or alloys are phosphatized in a bath containing NaF, Na silicate solution, and  $NaHCO_3$ , in addition to the usual phosphatizing components.

59. Shiraishi, Y. and M. Shiraishi  
LIGHT-FAST COLORING OF ALUMINUM AND  
ALUMINUM ALLOYS. Japan Patent 4462. 30 May 1959.

Aluminum or an aluminum alloy is electrolyzed to form the oxide film on the surface. The coated surface is immersed in an aqueous natural solution of ferric oxalate,

acetate, tartrate, succinate, phenolate, or ferric ammonium citrate to form a stable colored film.

60. Société Continentale Parker, Paris, France  
CHROMATING ALUMINUM. French Patent  
1,215,762. 15 Nov 1958.

A chromating solution for aluminum and its alloys containing hexavalent Cr,  $\text{PO}_4$  and F.

61. Spencer, L. F.  
Conversion coatings: chromate films. METAL  
FINISHING 58(1):58-65. 1960

The characteristics and uses of chromate conversion coatings and their application to... aluminum... are discussed. Chromate films give corrosion protection similar to phosphate coatings under paint. Chromate films are softer than phosphate coatings, but are self-sealing.

62. Spooner, R. C. and D. P. Seraphim  
Nickel-chromium plated aluminum sheet. METAL  
FINISHING 58(12):40-44. Dec 1960.

Atmospheric corrosion resistance of 3S Al alloy panels plated with bright chromium (Cu-Ni-Cr deposit) after pretreatment with phosphoric acid anodizing, zincate or Vogt processes.

63. Steinbrecher, L.  
CHROMATE CONVERSION COATINGS ON ALUMINUM.  
(Assigned to Amchem Products, Inc., Ambler, Pa.)  
U.S. Patent 3,009,842. 21 Mar 1960.

In the solutions used for forming chromate conversion coatings on aluminum, such as those containing hexavalent chromium, a F compound, and a soluble ferricyanide salt as disclosed in U.S. Patent 2,796,370-1, equally satisfactory results are obtained if some or all of the ferricyanide salt is replaced by the phospho- or silicomolybdic acids or their salts. If the solution contains 0.04-2.0 g. molybdenum in this form/l., the color of the coating is yellow, and with 3.5-6.0 g. it is good. Suitable solutions

may be formed by dissolving/gal. water, 0.4-5.0 oz. of a dry mixture containing hexavalent chromium 60-75, F compound, 8-20, and soluble heteropolymolybdic compound 4-20%. Suitable heteropolymolybdic compounds are  $\text{Na}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{Na}_3\text{PMo}_{18}\text{O}_{62}$ .  $\text{Na}_3\text{P}_2\text{Mo}_{12}\text{O}_{41}$  is also suitable, but not molybdic acid or its salts.  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  is suitable as well as its Na salt. An aluminum-base alloy was coated by 3 minute immersion at 75° F in various solutions each containing 5 g.  $\text{CrO}_3$  and 1 g.  $\text{HF}/1.$ , and, respectively, 0.1-8.0 g.  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . All were completely resistant to 20%  $\text{NaCl}$  solution fog for 500 hours.

64. Storace, G.

The use of elastomers for aluminum alloy protection. *PITTURE E VERNICI* 36:317-322. 1960. (In Italian).

Resistance tests towards sea water, acid, and alkali, solvents, resistance to stray currents, bending and impermeability tests have been made on elastomer-coated aluminum alloy sheets. The suitability of elastomers for protection of aluminum alloy surfaces has been ascertained.

65. Stricklen, R.

Finishing die-castings. V.--Chromate conversion treatments. *PRECISION METAL MOLDING* 16(6):43-45. 1958.

Flow-sheets are shown and pretreatments and processes for... aluminum... are outlined. Costs and properties are summarized.

66. T. E. C. A. (Traitements electrochimiques de l'aluminum), France. PROTECTION OF CHEMICALLY OXIDIZED ALUMINUM AND LIGHT-ALLOY ARTICLES. French Patent 1,199,070. 11 Dec 1959.

The treated articles are immersed immediately after rinsing in a 40% aqueous emulsion of a mixture of 50-80% of a methacrylic-acrylic and 20-50% of a vinyl chloroacetate copolymer. A compound for the absorption of ultraviolet radiation having the formula  $\text{C}_{18}\text{H}_{16}\text{N}_2$ , in an amount sufficient to give a concentration of 0.1-0.2% in the film after drying, may be added to the acrylic copolymer before polymerization.

67. Walker, H.  
Surface treatment of aluminum. PRODUCTS  
FINISHING 21(1):44-54. 1956.

A review of methods for electropolishing, chemical polishing, anodizing and sealing treatments for aluminum and its alloys is given.

68. Wernick, S. and R. Pinner  
Surface treatment and finishing of light metals.  
V. Chemical conversion coatings. METAL  
FINISHING 52(10):68-73; (11):83-87. 1954.

While the oxide conversion coat can be used without further treatment, in the main its function is to act as an undercoating and a base for organic finishes. It is normally considerably thinner than the oxide film produced by anodizing and for most protective applications the conversion coatings are, therefore, hardly competitive with anodic finishes. The main attraction of finishes obtained by chemical conversion is the economy and speed with which they can be produced. While aluminum is immersed in boiling water, the natural oxide film is increased in thickness, though only to a limited degree. The oxidation of aluminum in the presence of water will, however, stop after a certain thickness is reached, as the coating is non-porous and will not allow the passage of the solution to the metal surface. To obtain thicker coatings it is necessary, therefore, to include in the solution compounds which will have a slight dissolving action on the coating and facilitate entry of the solution. Commercially available solutions consist of inhibited alkaline solutions of weak acids such as HF,  $\text{H}_2\text{SiF}_6$ ,  $\text{H}_2\text{CrO}_4$ , or  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . The treatment is most effective when applied to aluminum and its alloys with Mg, Mn, and Si. On duraluminum-type and other high-Cu alloys, the coatings tend to be powdery. Effects of composition on color and nature of the coating are discussed in detail. The relation between operating conditions and film growth is discussed. Methods of dyeing the coatings are described.

69. Wernick, S. and R. Pinner  
Surface treatment and finishing of light metals.  
V. Chemical conversion coatings. 2. METAL  
FINISHING 53(2):66-72. 1955.

Various commercial processes for producing conversion coatings on light metals are described. These are the 2 Pylumin processes, one of which employs addition of  $\text{Na}_2\text{HPO}_4$  and the other the carbonate of a heavy metal; the Alrok process in which the treating solution contains  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  and is operated near the boiling

point for about twenty minutes. The coating obtained with this process is gray or green depending on alloy composition and operating conditions. A process has also been developed by which the Alrok coating is whitened by immersion in a solution containing  $\text{HNO}_3$  or a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Concentration and temperature are not critical. The Alodine or Alocrom process makes use of an acid solution containing chromates, phosphates, and fluorides, the optimum range being  $\text{PO}_4^{---}$  20–100 g./l.,  $\text{F}^-$  2.0–6.0 g./l., and  $\text{CrO}_3$  6.0–20.0 g./l., while the ratio of  $\text{F}^-$  to  $\text{CrO}_3$  lies between 0.18 and 0.36 with an optimum values of 0.27. Total acidity should not exceed 3N. The Alodine coating usually contains approximate Cr 18.2, Al 5.5, P 15.17, and F 0.2%. One of the advantages of the process is that it can be applied at room temperature, 65° F, in the short time of five minutes or at 120° F, in 1-1/2 minutes. Other chemical conversion processes described briefly are the Jirotko, Pacz, Protal, and McCulloch processes. Electrodeposited coatings can be applied over chemical conversion coatings.

70. Wernick, S. and R. Pinner  
Surface treatment and finishing of light metals.  
V. Chemical conversion coatings. SHEET  
METAL INDUSTRIES 27:71–81, 355–362,  
553–557. 1950.

A review dealing primarily with aluminum and its alloys.

71. Woldt, G.  
Chromizing of nonferrous metals. (Ueber die  
Chromatierung von Nichteisenmetallen) WERK  
STOFFE UND KORROSION 12(8) :486–493.  
August 1961. (In German)

Appraisal of chromate process, including explanation of underlying theory (illustrated by experimental data) and of working conditions for production of differently colored coatings on... aluminum...

72. Yamasaki, Y. and H. Harimoto  
Darkening aluminum by boiling water containing  
silica. Study on blackening aluminum and its  
alloy by boiling water. METAL FINISHING  
SOCIETY OF JAPAN. JOURNAL 14(5):165–168.  
May 1963.

Darkening aluminum by boiling water containing silica was investigated. Silica was added to water as Na silicate, which did not affect the degree of darkening and the

tone of surface color, when the ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  was 2:1, 1:1, or 1:2. Addition of  $\text{CaSO}_4$ ,  $\text{ZnSO}_4$  or  $\text{ZnW}_3$  to An silicate solution promoted darkening and a black surface was obtained. X-ray tests showed that the surface film formed in boiling water was amorphous. Only a film formed in boiling distilled water showed a weak diffraction pattern of boehmite. From the result of the test of calcining films at  $1,300^\circ\text{C}$  it was found that the film formed in the water containing silica had a  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  pattern, and that formed in  $\text{SiO}_2$ -Ca salt solution and well-water a mixture of  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . It seemed, therefore, that silica,  $\text{CaCO}_3$  and  $\text{CaSO}_4$  would be absorbed to hydrated aluminum oxide, and absorption of silica might be considered the most important factor in darkening.

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